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Effect of Pt Addition on Microstructure and Superconducting Properties for Filamentary (Nd,Sm,Gd)-Ba-Cu-O Superconductors

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***Abstract*—The filamentary $(Nd_{0.33}Sm_{0.33}Gd_{0.33})_{1.18}$-$Ba_{2.12}Cu_{3.09}O_y$ (NSG123) superconductors chemically doped with nominal Pt concentrations from 0 to 0.5 at% were fabricated by a solution spinning method. We investigated effects of the amount of Pt addition and cooling rate from partial melting temperature of 1050 °C during OCMG processing on superconducting properties and microstructure of filamentary samples. Pure NSG123 filaments cooled at 20 °C/h–50 °C/h showed the J_c vale higher than 2.0×10^4 A/cm^2 at 77 K and 0 T. Although the sample treated at fast cooling rate of 60 °C/h exhibited the J_c value of about 3.0×10^3 A/cm^2 at most, the NSG123 doped with 0.05 at% Pt cooled at 60 °C/h showed high J_c value of 2.0×10^4 A/cm^2 at 77 K and 0 T. The field dependence of transport J_c value was also investigated at 77 K for samples cooled at 60 °C/h. The J_c value of 0.8×10^4 A/cm^2 was maintained up to magnetic field of 5 T for the 0.05 at% Pt doped sample. The size of $(Nd, Sm, Gd)_2BaCuO_5$ particles in NSG123 matrix was reduced from about 3 to 0.5 μm with increasing Pt concentration from 0 to 0.5 at%. In addition, the connectivity in microstructure was improved with increasing Pt concentration. It was found that both J_c–B properties and the microstructure for the sample treated at fast cooling were effectively improved by Pt doping.**

***Index Terms*—Critical current density, magnetic field behavior, NSG-Ba-Cu-O filament, Pt chemical doping.**

I. INTRODUCTION

RE-Ba-Cu-O (RE: Rare Earth; RE123) wire and tape with high critical current density (J_c) and irreversibility field at 77 K has been developed for practical high-field power application such as power transition line, superconducting magnet and flywheel energy storage system. In several studies, the oxygen-controlled-melt-growth (OCMG) processed $LREBa_2Cu_3O_y$ (LRE: Light Rare Earth = Nd, Sm, Eu, Gd; LRE123) superconductors with $LRE_{1+x}Ba_{2-x}Cu_3O_y$ solid solution (LRE123ss) has attracted attention due to high critical temperature (T_c) and good J_c–B behavior compared with those of Y123 superconductor [1]–[3]. Especially, the ternary superconductors with different LRE elements showed advantages of high T_c, J_c and irreversibility field [4], [5].

Recently, we reported that the filamentary $(Nd_{0.33}Sm_{0.33}Gd_{0.33})_{1.18}Ba_{2.12}Cu_{3.09}O_y$ (NSG123) superconductors treated at optimum cooling rate showed high J_c value of 3.0×10^4 A/cm^2 at 77 K and 0 T [6]. However, it is required to establish the simple and fast formation technique for high quality LRE123 superconductors, since the superconductivities are strongly depended on the melt-processing condition, especially cooling rate from partial melting temperature. We have attempted to fabricate the filamentary samples with superior J_c properties even which prepared by low cost technique in a short time. Considering this purpose, platinum doping might be expected to obtain high quality filamentary NSG123 samples. In the case of Y123, it was reported that Pt doping influenced the Y_2BaCuO_5 (Y211)/liquid interfacial energy and/or the diffusivity of Y-element between Y211 particle and liquid phase in melt [7].

In this study, we have examined the effect of platinum doping on superconducting properties and microstructure for filamentary NSG123 superconductors prepared by a solution spinning method. The field dependence of transport J_c at 77 K for filamentary NSG123 superconductor doped with 0.05at% is also investigated.

II. EXPERIMENTAL PROCEDURES

Filamentary superconducting samples were fabricated by a solution spinning method as described elsewhere [8]. The precursor NSG123 filaments with starting composition of Nd : Sm : Gd : Ba : Cu = 0.39 : 0.39 :0.39 : 2.12 : 3.09 was synthesized from a homogeneous aqueous solution containing metal acetates of Nd, Sm, Gd, Ba and Cu, poly (vinyl alcohol), propionic acid and 2-hydroxy isobutyric acid. Various amounts of Pt ranging from 0.05 to 0.5 at% using hydrogen chloroplatinic acid hexahydrate, $H_2PtCl_6 \cdot 6H_2O$ relative to NSG123 were also added into an aqueous solution, and thoroughly mixed. After condensation to obtain a stable viscous homogenous spinning dope, the dope was extruded through the stainless nozzle as a filament shape into a hot air zone, and coiled on a winding drum. The precursor filament was heated to 450 °C at a heating rate of 25 °C and then calcined at 900 °C for 15 min in flowing pure O_2 to remove extra components such as Cl_2 and CO_2. The calcined sample was partially melted at 1050 °C for 30 min in flowing $0.1\%O_2+Ar$. Then, the sample was cooled in two steps, first cooling step from partial-melting temperature of 1050 °C to 910 °C at a rapid rate of 60 °C/h and second step from 910 °C

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TABLE I
THE CRITICAL CURRENT DENSITY AT 77 K AND SELF-FIELD AND ELECTRICAL PROPERTIES FOR FILAMENTARY NSG123 SUPERCONDUCTORS

sample	Cooling rate (°C/h)	J_c ($\times 10^4$ A/cm^2)	T_c (K)	ΔT_c (K)
NSG123	20	2.7	91.3	0.8
	60	0.3	91.8	2.2
NSG123 +0.05 at% Pt	20	1.6	91.2	1.8
	60	2.0	92.3	1.8

to 500 °C was at a cooling rate of 50 $^\circ$C/h. The oxygenation of the sample was carried out by a two-step treatment, which was at 500 °C for 5 h and 340 °C for 10 h in flowing pure O_2 gas.

The T_c and transport J_c were measured by a standard DC four-probe resistive method. Silver paint was used to connect the silver sputtered parts of the sample to Ag electrodes of 100 μm in diameter for supplying DC currents and Ag electrodes of 75 μm in diameter for voltage leads. The sample was embedded on the substrate at the arbitrary direction for the sample diameter using epoxy resin and mounted on a critical-current-measuring holder. The external magnetic field was always applied in a direction perpendicular to the filament length using a high homogenous 20 T superconducting magnet at the High Field Laboratory for Superconducting Materials, Tohoku University. The pulse current was passed along the direction of the filament length and perpendicular to the applied magnetic field. The J_c was defined by the offset method from the point on the I–V curve at which the voltage of 1 μV appeared between voltage terminals separated by 2 mm. The microstructure of the sample was also studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray (EDX). In addition, the decomposition temperature of filamentary samples was examined using the differential temperature analysis (DTA).

III. RESULTS AND DISCUSSION

We initially investigated the effect of cooling rate from partial melting temperature of 1050 °C to 910 °C on transport J_c value of pure NSG123 sample and NSG123 doped with 0.05 at% Pt sample. Table I summarizes the transport J_c value at 77 K and 0 T, T_c, transition width ΔT_c of filamentary samples cooled at either 20 $^\circ$C/h or 60 $^\circ$C/h. Filamentary NSG123 superconductors without Pt doping cooled at 20 $^\circ$C/h shows the J_c value higher than 2.7×10^4 A/cm^2, contrast to the J_c value of 3×10^3 A/cm^2 for the sample treated at 60 $^\circ$C/h. On the other hand, 0.05 at% Pt doped sample cooled at 60 $^\circ$C/h exhibits the J_c value higher than 2.0×10^4 A/cm^2. This sample shows also high T_c value and sharp ΔT_c compared with those of pure sample treated at same cooling condition. It is clearly found that the J_c value and electrical properties of filamentary NSG123 superconductor treated at fast cooling is improved by Pt doping. Therefore, the superconducting properties and microstructure of Pt doped filamentary NSG123 superconductors treated at fast cooling rate of 60 $^\circ$C/h are hereafter measured and described.

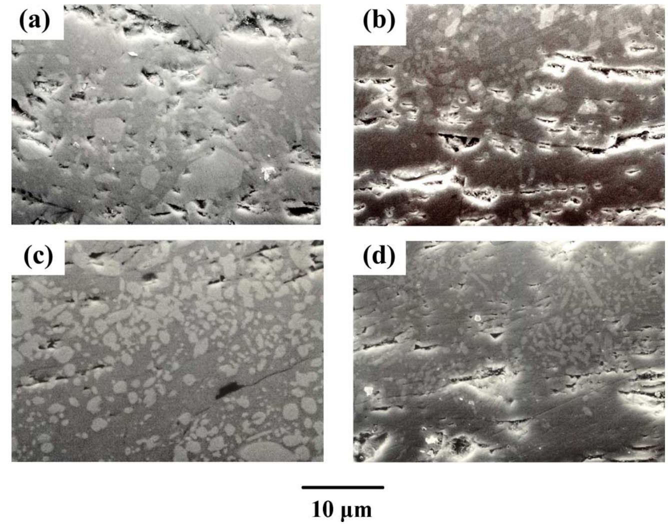

Fig. 1. SEM photographs of the polished surface on the longitudinal cross-section for pure NSG123 (a), NSG123+0.05 at% Pt (b), NSG123+0.1 at% Pt (c), and NSG123+0.5 at% Pt (d).

Fig. 1 shows typical SEM photographs of the polished surface on the longitudinal cross-section of filamentary NSG123 superconductors doped with various content of Pt. From SEM photographs of fracture surface, it was confirmed that the microstructure became dense and the texture aligned along the filament direction with increasing Pt content. The light contrast particles in these photographs were identified the NSG211 phase by EDX analysis. Each sample has a large number of NSG211 particles in NSG123 matrix. It should be noted that the NSG211 particles finely dispersed in matrix of the sample doped with Pt. This is consistent with previous report that the size of the Y211 particles in Y123 matrix decreases with increasing Pt content [9].

DTA measurement in $0.1\%O_2 + \mathrm{Ar}$ atmosphere was carried out to understand the decomposition temperature of these samples. DTA result showed that the decomposition temperature of filamentary NSG123 samples doped with 0, 0.05, 0.1 and 0.5at% were 1020 °C, 1013 °C, 1014 °C, and 1006 °C, respectively, indicating that the decomposition temperature decreased with increasing Pt concentration. This would be provided that the NSG123 crystal growth was promoted through peritectic reaction for filamentary samples doped with Pt.

Fig. 2 shows relationship between the temperature and resistivity of filamentary samples cooled at 60 $^\circ$C/h. All samples show metallic behavior from room temperature to transition onset, and then resistivity rapidly decreases to zero. The sample doped with 0, 0.05, 0.1 and 0.5 at% Pt show the T_c value of 91.8, 92.3, 93.4 and 93.0 K, and transition with ΔT_c of 2.2, 1.8, 0.8 and 1.5 K, respectively, The T_c and ΔT_c value are improved when Pt doping level is lower than 0.1 at%. Experimental results dealt with the effect of cooling rate from partial melting temperature of 1050 °C on superconducting properties of pure filamentary NSG123 superconductors were shown in previous paper [6]. We reported that the sample cooled at 60 $^\circ$C/h showed the T_c of 91.8 K and broad ΔT_c value of 2.2 K which were inferior to those of 40 $^\circ$C/h cooled sample with high J_c value of 3×10^4 A/cm^2, because of the large size NSG211 particles

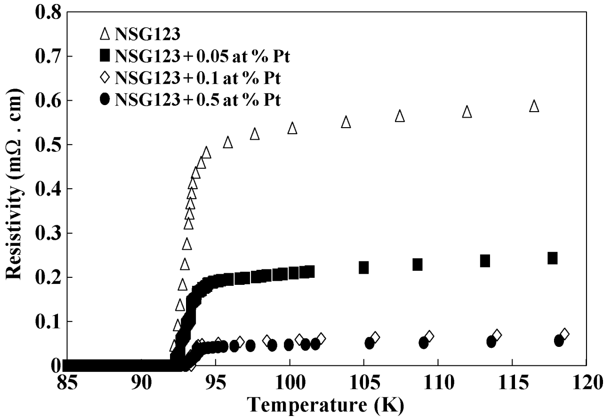

Fig. 2. Resistivity as a function of temperature for the filamentary samples.

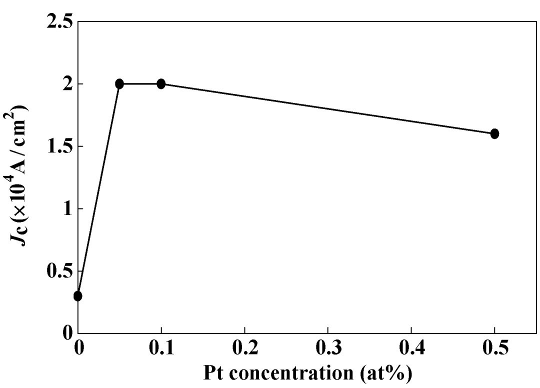

Fig. 3. The relationship between the transport J_c and Pt content in filamentary NSG123 superconductors.

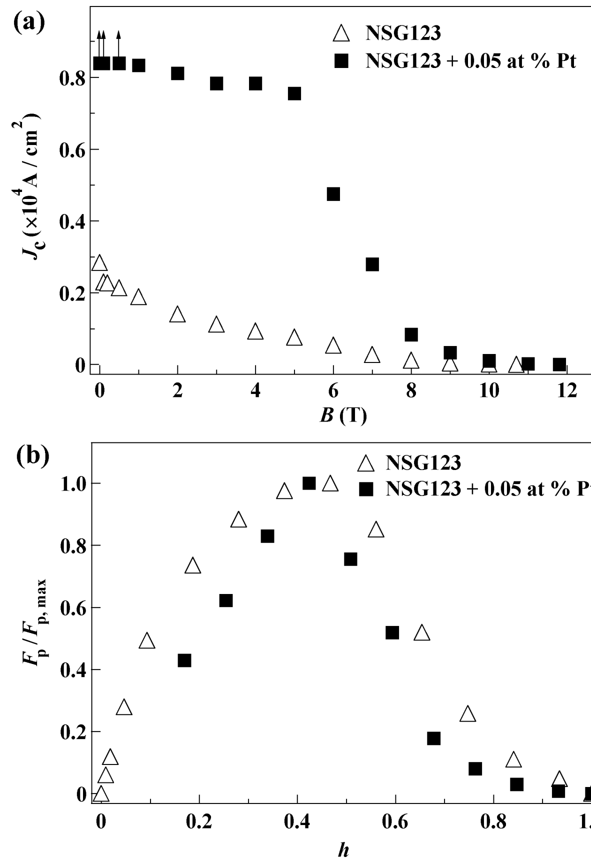

Fig. 4. The field dependence of transport J_c at 77 K for pure sample and 0.05at% Pt doped sample (a), and volume pinning force $F_p/F_{p,max}$ as a function of deduced field $h = H_a/H_{irr}$ (b).

in NSG123 matrix, oxygen deficiency and poor connectivity in the 60 $^\circ C/h$ sample. In the case of present study, it is confirmed from Fig. 1 that the NSG211 particles are refined with increasing Pt content. Hence, the improvement of the T_c value and ΔT_c value might be caused by an improvement of oxygen defect. In addition, the resistivity at 100 K of present samples decreases with increasing Pt content, suggesting that the connectivity enhanced.

Fig. 3 shows transport J_c at 77 K and 0 T as a function of the Pt concentration in filamentary NSG123 superconductor cooled at 60 $^\circ C/h$. The J_c value of pure NSG123 sample is $3.0 \times 10^3\ A/cm^2$ at most. It should be noted that the 0.05–0.1 at% Pt doped samples show high J_c value of $2.0 \times 10^4\ A/cm^2$, which is about seven times larger than that of pure NSG123 sample. From these results, it is clearly found that 0.05 or 0.1 at% Pt doping is effective in enhancement of transport J_c at 77 K and 0 T for filamentary NSG123 superconductor treated at rapid cooling of 60 $^\circ C/h$. We also confirmed that the dense microstructure and finely dispersed NSG211 particles in NSG123 matrix, and high T_c value and sharp ΔT_c for 0.05 and 0.1 at% Pt doping samples.

The field dependence of transport J_c for filamentary samples was examined in an applied magnetic field. Fig. 4(a) shows the J_c at 77 K as a function of applied magnetic field for the pure sample and 0.05 at% Pt doped sample cooled at 60 $^\circ C/h$. The sample was embedded on the substrate at the arbitrary direction for the sample diameter, the external magnetic fields were applied in direction in parallel to the substrate surface where the sample was embedded. Because samples were sometimes burnt out by applying the current larger than 0.5 A, critical current I_c value was stopped at the limit of 0.3 A in J_c–B measurement.

Therefore, the arrow in this figure implies J_c value higher than the value when current of 0.3 A is applied. The J_c value of pure sample gradually decreases with increasing applied magnetic field. On the other hand, the J_c value of $8 \times 10^3\ A/cm^2$ can be maintained with little degradation in magnetic field up to about 5 T for the 0.05 at% Pt doped sample. While the J_c value decreases by applying the magnetic field higher than 5 T, the irreversibility field of about 12 T can be obtained. It should be noted that distinct difference in J_c–B behavior was observed at intermediate magnetic fields between the 0.05 at% Pt doped sample and the pure sample. Inoue *et al.* have reported that the J_c value enhanced in intermediate magnetic field for the bulk Dy123 sample including large size Dy211 particles with a large number of oxygen defects which effectively play in pinning contribution [10]. Furthermore, it is also reported that the $Ba_4CuPt_2O_9$ (0412) compound is formed in bulk Y123 superconductor with Pt [11]. Unfortunately, we could not detect any trace of 0412 compounds in our samples doped with Pt by neither XRD nor EDX analysis, because the particle size was presumably too small and additional Pt concentration was rather low. The 0412 compounds might exist in our sample doped with Pt as well as the bulk Y123 superconductors with Pt. $NSG_{1+x}Ba_{2-x}Cu_3O_y$ solid solution (NSG123ss) with small x value is also useful for enhancing the J_c value. Therefore, 0.05 at% Pt doped our sample with small NSG211 particles shows high J_c value in low and intermediate magnetic field due to synergy effect of the oxygen defect, fine second phase, NSG123ss, etc.

In order to study what kinds of flux pinning center act, we examined flux pinning mechanism based on an analysis of the normalized volume pinning force at the reduced field. Normalized volume pinning force density, $F_p/F_{p,max}$ ($F_p = J_c \times H_a$) as a function of reduced field, $h = H_a/H_{irr}$ is also shown in Fig. 4(b), where H_a is the applied magnetic field and H_{irr} for both samples measured at 77 K is the irreversibility field which obtained from J_c–B behavior using the criterion 10 A/cm^2. The peak position of pure sample locate at $h = 0.47$. This peak position is close to $h = 0.5$, which is theoretically predicted for $\Delta\kappa$ pinning due to compositional fluctuation of NSG123ss cluster [12]. In contrast, 0.05 at% Pt doped sample shows peak position of $h = 0.42$, which is medium position and predicted that the pinning contribution may be mixture of $\Delta\kappa$ pinning and normal core pinning [13]. It should be noted that the peak position shifts to lower h position by Pt doping. It is suggested that the dominant pinning replaces from $\Delta\kappa$ pinning to normal pinning when the Pt is doped in filamentary NSG123 superconductors. As seen in SEM observation in Fig. 1, fine NSG211 particles in NSG123 matrix were dispersed in Pt doped sample compared with that of pure sample. Therefore, it might be explained that the amount of the effective size NSG211 particles increased. In addition, in case of the Pt doped sample, perhaps normal pinning such as the 0124 phase and the compounds with Pt may be one of the effective pinning [11].

IV. Conclusion

We studied the influence of Pt doping on superconducting properties and microstructure of filamentary NSG123 superconductors. The filamentary NSG123 superconductors doped with nominal Pt concentration between 0 and 0.5 at% were prepared by a solution spinning method. Although the J_c value of pure NSG123 superconductors treated at fast cooling rate of 60 °C/h was 3.0×10^4 A/cm^2 at most, 0.05 and 0.1 at% Pt doped filamentary NSG123 superconductors exhibited high J_c value of 2.0×10^4 A/cm^2 at 77 K and 0 T. The enhancement of J_c–B behavior was also observed in low and intermediate magnetic field for NSG123+0.05 at% Pt sample. The filamentary NSG123 superconductor doped with Pt showed the dense and aligned microstructure with finely dispersed NSG211 particles.

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